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ANALYSIS OF MERCURY IN SIMULATED NUCLEAR WASTE (U)

by

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INTRODUCTION

Mercury, Hg, is a non-radioactive component in the High Level Waste at the Savannah River Site (SRS). Thus, it is a component of the Defense Waste Processing Facility's (DWPF) process streams. It is present because mercuric nitrate ($Hg(NO_3)_2$) is used to dissolve spent fuel rods.[1] Since mercury halides are extremely corrosive, especially at elevated temperatures such as those seen in a melter (1150°C), its concentration throughout the process needs to be monitored so that it is at an acceptable level prior to reaching the melter off-gas system. The Hg can be found in condensates and sludge feeds and throughout the process and process lines, *i.e.*, at any sampling point. The different sample types that require Hg determinations in the process streams are: 1) sludges, which may be basic or acidic and may or may not include aromatic organics, 2) slurries, which are sludges with frit and will always contain organics (formate and aromatics), and 3) condensates, from feed prep and melter off-gas locations. The condensates are aqueous and the mercury may exist as a complex mixture of halides, oxides, and metal, with levels between 10 and 100 ppm. The mercury in the sludges and slurries can be Hg^0, Hg^{+1}, or Hg^{+2}, with levels between 200 and 3000 ppm, depending upon the location, both time and position, of sampling. For DWPF, both total and soluble Hg concentrations need to be determined. The text below describes how these determinations are being made by the Defense Waste Processing Technology (DWPT) Analytical Laboratory at the Savannah River Site. Both flame atomic absorption (FAA) and cold vapor atomic (CVAA) measurements are discussed. Also, the problems encountered in the steps toward measuring Hg in these sample types of condensates and sludges are discussed along with their solutions.

EXPERIMENTAL

Simulated non-radioactive waste samples from the pilot process known as IDMS, Integrated DWPF Melter System, Fig. 1, were analyzed for Hg by both FAA and CVAA. The samples consisted of condensates and sludges. Both sample types required sample preparation before analyses. The Analytical Services Group (ASG), Analytical Development Section (ADS), of the Savannah River Laboratory (SRL) provided the basic method procedure for sample preparation.[2,3]. However, this particular procedure[3] was modified

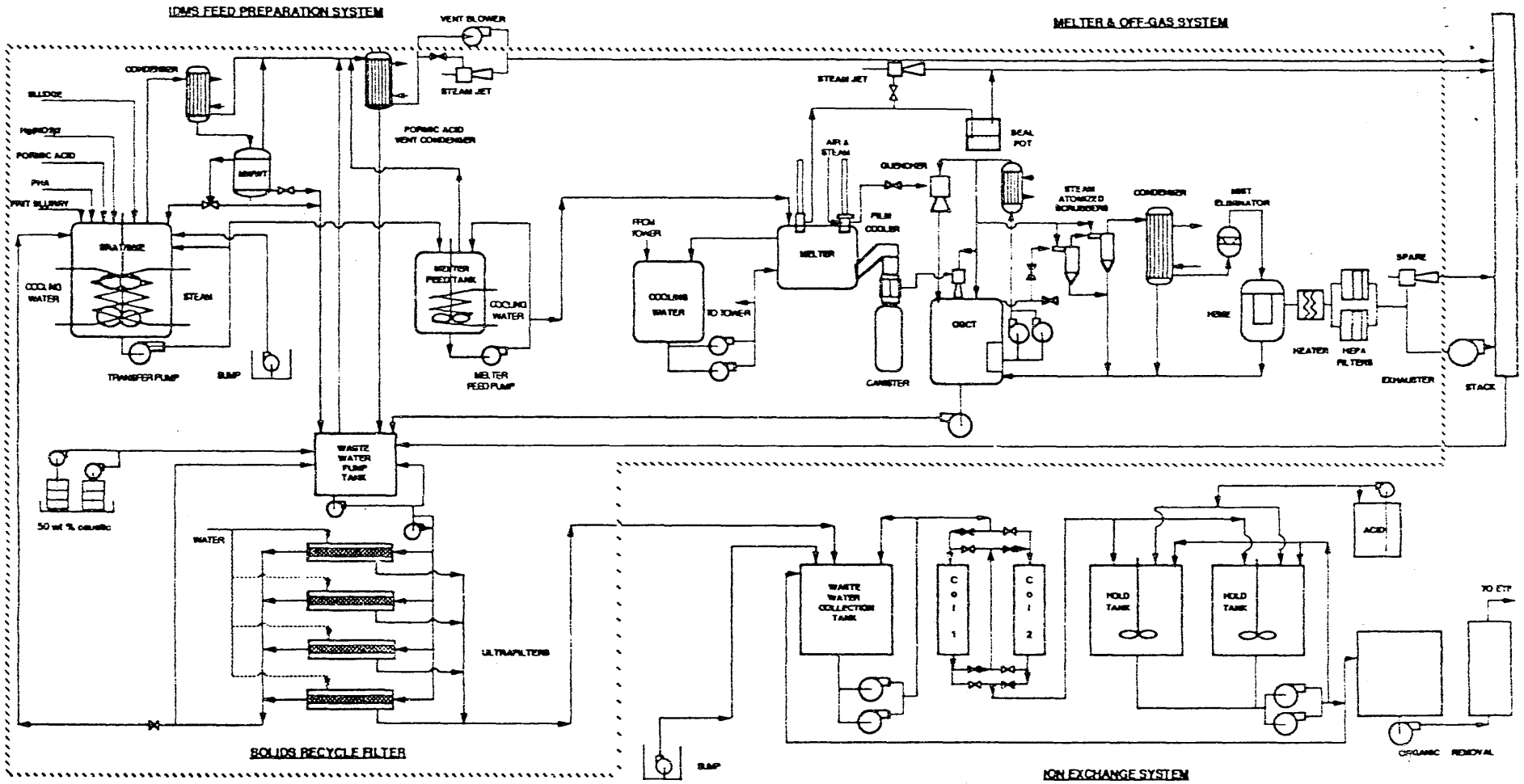


Figure 1: IDMS Process Schematic

for use on these non-radioactive samples in this non-regulated, non-radioactive lab.

The procedure uses 15 mLs of sample, in a 50 mL centrifuge tubes, to which is added 5 mLs each of concentrated HCl and concentrated HNO_3. The sample/acid mixture is then heated in a Blue M drying oven at 95 ± 5°C for 2 hours, with an intermediate swirl mixing. A dilution of this sample/acid mixture into distilled, deionized (dH_2O) is required before measurement by flame atomic absorption (FAA). A larger dilution is required for CVAA measurement. All volumes of sample, acids, and dilutions were determined through the use of calibrated pipets and by weight. All determinations were thus performed as weight/weight ppm. The spectrometer used for the flame measurements was a Varian AA-400 and that used for the CVAA measurements was a Varian AA-10 (Figs. 2A+2B) with the vapor generation assembly-76 (VGA). Aqueous standards, blank, 20 ppm, and 50 ppm, were used for the FAA calibration while a blank, 10 ppb, 20 ppb, and 50 ppb were used for CVAA calibration. Measurements for both setups were performed at 253.7 nm with a 0.5 nm spectral band pass. A 10 cm absorption cell was used in CVAA with nitrogen as the carrier gas and stannous chloride ($snCl_2$) as the reductant. An air-acetylene flame was used for FAA.

RESULTS

The following table summarizes the method comparison results for 2 of the samples.

Sample #	Analysis Method (AM)						Units
	1	2	3	4	5	6	
1	96.7	89.2	147.0	97.5	7.3	6.4	ppm
2	80.4	72.1	124.9	82.8	6.0	5.6	ppm

where AM 1 = HCl/HNO_3 1:1, dilution by wt, FAA
where AM 2 = HCl/HNO_3 1:1, dilution by wt, FAA, #2
where AM 3 = HCl/HNO_3 1:1, dilution by volume, FAA
where AM 4 = HCl/HNO_3 1:1, dilution by volume, density corrected, FAA
where AM 5 = HCl/HNO_3 1:1, dilution by wt, density corrected, CVAA
where AM 6 = HCl/HNO_3 1:1, dilution by wt, density corrected, CVAA

and AM 2 was simply a second sample treated identical to AM 1, as was

Figure 2A: Varian AA-400.

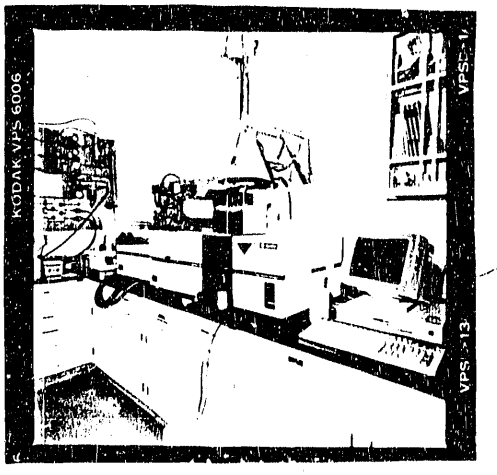
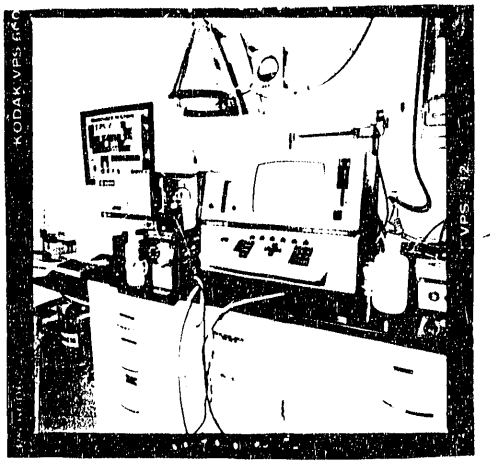


Figure 2B: Varian AA-10 with VGA-76.



AM6 for AM 5, and was used for control purposes.

DISCUSSION

This procedure, unfortunately, does not provide a complete dissolution of the sludges. However, the Hg, along with other easily dissolved elements, such as sodium, potassium, etc., should be totally in solution. Furthermore, the oxidizing strength of the 1:1 HCl and HNO3 is sufficient to ensure that all of the Hg is Hg^{+2}. If the Hg is not all in the same state, the following may be factors in FAA measurements: 1) Hg^{+1}, or Hg^{+2} have different sensitivities in the air-acetylene flame with Hg^{+1} being more sensitive, and 2) Hg^0, Hg^{+1}, or Hg^{+2} have different atomization efficiencies with Hg^0 being 100%.[4] Also, in FAA, the entire sample/acid mixture is aspirated which can produce interference effects with the measurements. These problems do not exist in CVAA. Here, all that is detected is Hg^0 since it should be the only analyte absorbing at 253.7 nm through the absorption cell by the nitrogen. However, if there are other metal ions present that are reduced by $SnCl_2$ they can amalgamate with the Hg and prohibit its detection.[4]

The density of the undiluted sample/acid mixture, for the samples used in this study, was about 1.30. This proved to be a contributing factor in providing accurate measurements for the Hg determinations, since the standards all had densities, for all practical purposes, of 1.00. This density difference was the sole drive to make all measurements and dilution corrections by weight. Aliquots used for second dilutions had densities of about 1.16. These 2 density factors were used to compute column 4 in the result table above.

The sludges containing aromatic organics proved problemsome from the standpoint of safety during the sample preparation. The procedure is optimal for Hg recovery when the centrifuge tubes are tightly sealed during the heating stage. However, with the presence of the organics, which include benzene, phenol, diphenyl, diphenylamine, terphenyl, etc., there is a substantial amount of pressure buildup in the tubes. This pressure is great enough to force the caps off of the tubes allowing the possibility of sample release inside of the oven. This was observed using both polyethylene tubes and caps as well as polysulfone tubes with sealing caps. Two solutions were proposed: 1) use teflon microwave vessels and 2) not tightly seal the tubes. The downfall of the first is that the teflon is not transparent, making aliquot removal via pipet difficult, since the dissolution is not COMPLETE for the sludge samples. The disadvantage

to the second solution is that there must be a mechanism to correct for possible sample evaporation during the heat stage. This, however, was easily overcome by instituting pre- and post-weighings relative to the heating stage. Also, for these samples, there does not appear to be any loss of volatile Hg species in the heating stage when caps are firmly but not tightly capped. The volume loss, via weight measurements, of the 25 mL sample/acid mixture is about 0.3 mL, on average.

From the table above, the results from FAA are about 16 times higher than those from CVAA. The CVAA results are the most consistent with the offgas Hg balance and are assumed to be the correct values.[5] Since these samples were process samples and not spiked samples, the accuracy of the results can only be compared to what is expected from calculations, process history, and mass balance closures. The precision was quite good for all of the measurements, with respect to the individual methods, FAA and CVAA. Since all dilutions, which were at least 1 to 10, were made into dH_2O, the need for matrix matches standards should have been eliminated. This, however, may not be the case and will need further pursuit.

REFERENCES

1. R. E. Eibling. "Results of Mercury Reduction with Formic Acid", USDOE Report DPST-83-1047, Savannah River Site, Aiken, SC 29808 (1983)..
2. DPST-88-731, Determination of Mercury in DWPF Samples.
3. Procedure 772T-70207, 1:1 HNO_3/HCl Sample Preparation.
4. Varian Techtron Pty. Ltd. "Analytical Methods for Flame Spectroscopy" (1979).
5. N. D. Hutson, J. R. Zamecnik, et.al. "Integrated DWPF Melter System (IDMS) Campaign Report: Mercury Operations (U), WSRC-TR-91-0363, (1991).

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